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The constituents of the ink from a Qumran inkwell: new prospects for provenancing the ink on the Dead Sea Scrolls

Kaare Lund Rasmussen^{a,*}, Anna Lluveras Tenorio^b, Ilaria Bonaduce^b, Maria Perla Colombini^b, Leila Birolo^c, Eugenio Galano^c, Angela Amoresano^c, Greg Doudna^d, Andrew D. Bond^a, Vincenzo Palleschi^{e,f}, Giulia Lorenzetti^{e,g}, Stefano Legnaioli^e, Johannes van der Plicht^{h,i}, Jan Gunneweg^j

^a Institute of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark

^b Dipartimento di Chimica e Chimica Industriale, Via Risorgimento 35, 56126 Pisa, Italy

^c Dipartimento di Chimica Organica e Biochimica, Università degli Studi di Napoli Federico II, Napoli, Via Cinthia, I-80127, Italy

^d Columbia College, 13910 45th Avenue NE #802, Marysville, WA 98271, USA

^e Institute of Chemistry of Organometallic Compounds of CNR, Applied Laser Spectroscopy Laboratory (ALS-ICCOM), Area della Ricerca del CNR, Via G. Moruzzi 1, I-56124 Pisa, Italy

^f University of Pisa, Department of Archaeology, Via Galvani 1, Pisa, Italy

^g University of Florence, Department of Chemistry, Via della Lastruccia 1, Sesto Fiorentino, Italy

^h Center for Isotope Research, Nijenborgh 4, 9747 AG Groningen, The Netherlands

ⁱ Faculty of Archaeology, Leiden University, P.O. Box 9515, 2300 RA Leiden, The Netherlands

^j Institute of Archaeology, Hebrew University of Jerusalem, Mount Scopus, 91905 Jerusalem, Israel

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ABSTRACT

A unique sample of ink from an inkwell in the Schøyen Collection allegedly found at Qumran has been subjected to analyses by several analytical techniques: GC–MS, proteomic analysis, PXRD, Raman, (ATR) FT-IR, LIBS, ICP–MS and MS. The results reveal to an unexpected level of detail how the ink was manufactured, which gives insight into the industrial processes and craftsmanship that were practiced at the Qumran settlement during the Second Temple period (100 BCE–CE 70). The identified minerals and other organic and inorganic materials are sufficiently multiple and diverse that it is probable that this specific ink can be recognized if analyses of inks are performed on manuscripts from Qumran and other locations in Israel and the Middle East. The present work exposes a distinct and unique possibility to shed light on early Jewish manuscript controversies, including their provenance.

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1. Introduction

In 1947–1955 a large quantity of fragmentary scrolls from approximately two thousand years ago was found in caves around Qumran near to the Dead Sea east of Jerusalem, amounting to over

* Corresponding author. Tel.: +45 28713709.

E-mail addresses: klr@sdu.dk (K.L. Rasmussen), anna.lluveras@for.unipi.it (A.L. Tenorio), ilariab@dcc.unipi.it (I. Bonaduce), perla@dcc.unipi.it (M.P. Colombini), birolo@unina.it (L. Birolo), eugenio.galano@unina.it (E. Galano), angela.amoresano@unina.it (A. Amoresano), gdoudna@msn.com (G. Doudna), adb@sdu.dk (A.D. Bond), vincenzo.palleschi@cnr.it (V. Palleschi), a_lorenzetti@hotmail.com (G. Lorenzetti), stefano.legnaioli@pi.iccom.cnr.it (S. Legnaioli), j.van.der.Plicht@rug.nl (J. van der Plicht), jan.gunneweg@huji.ac.il (J. Gunneweg).

nine hundred ancient Jewish, biblical and sectarian texts. Three-quarters of the texts were found in one cave, Cave 4, which can be accessed only from the site of Khirbet Qumran, thereby raising the question of whether the scrolls were actually written at the site. Due to the variety of kinds of scrolls and scribal hands, it has long been accepted that many of the scrolls must have been imported. However, following the interpretation of the excavator, Roland de Vaux (e.g. de Vaux, 1973), most scholars working on the texts today believe that at least some were written by the Qumran residents. While this seems plausible, it has so far remained unproven.

No scraps of parchment were found at the site—a fact commonly attributed to destruction by fire and/or water over time—but de Vaux reported finding three inkwells, two made of

clay and one made of bronze. Two of the inkwells were found in locus 30, commonly referred to as the “scriptorium” (Fig. 1), and one was found in an immediately adjacent room (Nir-El and Broshi, 1996). One further inkwell was found by another excavator of Qumran, Solomon Steckoll, in 1966–1967 (Steckoll, 1968, 1969; Goranson, 1993), and a fifth inkwell said to be from Qumran was bought by a private person in 1967 from Kando (Khalil Eskander Shahin), the antiquities dealer who also bought many of the Dead Sea Scrolls from the Bedouin (Goranson, 1992: 39). In 1994, Stephen Goranson published a sixth inkwell identified as coming from Qumran in the private antiquities collection of Martin Schøyen of Oslo (Goranson, 1994). This last inkwell (Fig. 2), referred to here as the Schøyen inkwell, is the subject of our present study.

Goranson reported that the Schøyen inkwell is “made of bronze and has two handles on top that turn in opposite directions. It is a little over three inches (ca 8 cm) high and the same in diameter. Its shape, however, differs from the other known Qumran inkwells” (1994: 39). According to Schøyen, “this inkwell was discovered in the Qumran ruins by Bedouin of the Ta’amireh tribe in about 1950, after the Qumran Cave 1 scrolls had come to light, but before Roland de Vaux began excavating the ruins in 1951”. According to Goranson Kando confirmed this account in 1993. Goranson noted that the number of inkwells found at Qumran is unusually high compared to reported results from other excavations, and concluded that the writing or copying done at Qumran “most likely produced some—though surely not all—of the Qumran manuscripts” (Goranson, 1994: 39).

According to Elgvin and Pfann (2002) the Schøyen inkwell was found together with a bronze incense altar. The antiques dealer Kando said that these two items were found together by the Bedouin at Khirbet Qumran “sometime before R. de Vaux and L. Harding started their preliminary excavations in November 1951”. Kando sold them to J. Allegro in 1953. John Allegro sold the two items to an anonymous private collector in 1963. Subsequent proprietors were Fayez Barakat, Los Angeles, 1975; Mathias Komor, New York, 1975; an anonymous collector until 1992; David Goldstein, Los Angeles, 1992; and finally Martin Schøyen, 1994. According to Elgvin and Pfann, Kando confirmed in 1993 that the inkwell and the altar indeed were the same as those found by the Bedouin at Qumran around 1950.

In 2002, tests carried out at the Norwegian Technical University of Trondheim showed that the bronze of the Schøyen inkwell comprised of 55–68 wt% Cu, 23–39 wt% Pb, and 5–8 wt% Sn. Traces of ink in the inkwell were also tested, but the stated results were



Fig. 1. Photo of locus 30 – the scriptorium – in the Qumran settlement (Photo: from Wikipedia). The Qumran settlement is situated on the western bank near the northern end of the Dead Sea (KML-link to Google Maps).



Fig. 2. The Schøyen inkwell, inventory number MS 1655/2 (Photo: From the Schøyen Collection home page).

only that the ink “was black, based on lamp-soot, as was the ink used at Qumran” (Elgvin and Pfann, 2002, no mention of the analytical techniques used). Previous analyses of inks from the Dead Sea Scrolls, for example that of Nir-El and Broshi in 1996, encountered difficulties in distinguishing the inorganic composition of the ink from that of the parchment, and the only conclusion drawn was that the ink was made of a “carbonaceous material”. Metals such as Cu and Pb were detected (Nir-El and Broshi, 1996), but it was concluded that these were contaminants from the walls of the inkwells. Further analyses by Rabin et al. (2009) and Mantouvalou et al. (2011), based on infrared spectroscopy and X-ray fluorescence (XRF) techniques, did not provide satisfactory identification of any binder in the ink, and significant uncertainty exists in the quantitative interpretation of their IR results. The proposal that Br from Dead Sea brine was used deliberately in the ink and that elevated Br-concentrations allow unique provenancing of ink to Qumran, as stated by Rabin et al. (2009) and Mantouvalou et al. (2011), seems somewhat speculative. There were large and multiple freshwater reservoirs available at Qumran, and it seems equally plausible that ink manufactured at Qumran would have used freshwater without elevated amounts of Br. The stated uncertainties and the relatively large inter-sample variations in the Br-data of Mantouvalou et al. (2011, Fig. 9) also do not provide statistically significant differences between the analyzed samples. As an alternative, it can be suggested that the Br found by Rabin et al. (2009) and Mantouvalou et al. (2011) could have come to the scrolls via sea spray, provided the manuscripts were stored near to the Dead Sea for a prolonged time. Until more comparative data are obtained concerning Br-levels on ink from other places than Qumran, e.g. Jericho and Jerusalem, we are not convinced that Br level provides an adequate provenancing tool.

In the present study we have analyzed the ink from the Schøyen inkwell using a wide variety of contemporary analytical techniques that can provide a detailed profile of both the organic and inorganic content. We pinpoint ten distinct characteristics which may provide a sufficient basis to match the ink from the Qumran inkwell to specific inks on the Dead Sea Scrolls or other manuscripts from the region.

2. Methods

2.1. Sampling

A solid sample was scraped out of the Qumran inkwell in the Schøyen Collection, MS 1655/2, by one of us (J. Gunneweg) using a scalpel and kept in a pre-cleaned plastic vial. Part of the sample was handed over to University of Southern Denmark, from where sub-samples were distributed to the other partners in pre-cleaned glass vials, or in some case in pre-cleaned plastic vials, taking care that the samples were not exposed to contamination. After a sample was exposed to a non-destructive analysis it was returned to University of Southern Denmark and from there sent out for the next analysis. At each instance the content of the vials were inspected and found in accordance with the description of the sample when it was sent out, in this way making sure that samples were not interchanged. A bulk sample of a few milligrams was photographed (Fig. 3) and subsequently used for Gas Chromatography–Mass Spectrometry analysis (GC–MS). Four morphologically distinct grain types can be identified in the sample. Characterized by their colour the four grain types are: white, black, green, and brown/black (see Fig. 3). The last type can also be described as black with rusty spots. Single grains of each of these four types ranging in size from 50 to a few hundred μm were subjected separately to non-destructive powder X-ray diffraction (PXRD), Raman and Fourier Transform Infrared (FT-IR) spectroscopy, and finally analyzed destructively by Laser-Induced Breakdown Spectroscopy (LIBS) analysis. A further set of 4 grains were analyzed by Induced Coupled Plasma Mass Spectroscopy (ICP-MS) and a single black grain was analyzed for protein identification. Finally two bulk samples of 8 and 22 mg of the remainder of the bulk ink sample were measured for stable carbon isotopes and subjected to attempts of radiocarbon dating by Accelerator Mass Spectrometry (AMS). A summary of the analyses performed is given in Table 1.

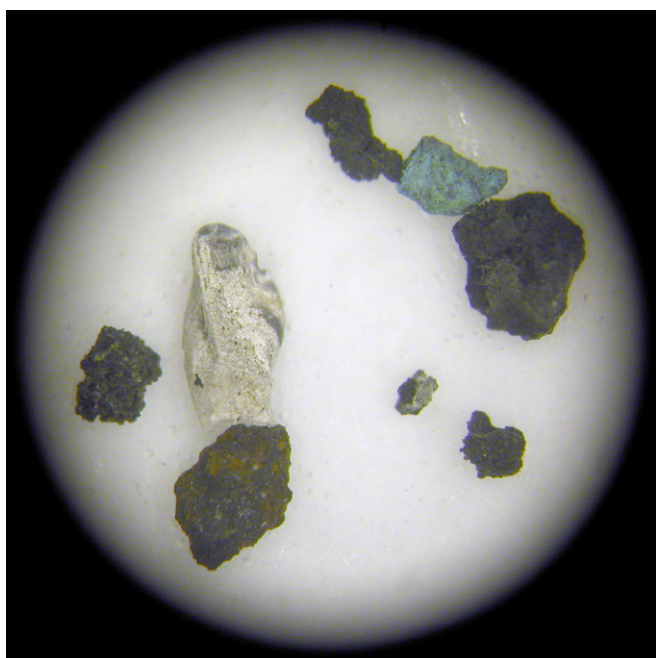


Fig. 3. Optical micrograph of the bulk ink sample prior to GC–MS analysis. The four distinctly different types of grain can be seen in this photo: the white, the black (5 pieces), the green, the black with brown spots. Field of view ca 4 mm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Sample numbers, description and analyses applied. KLR-8007 is a bulk sample taken from sample number QUM-435 in the records of Jan Gunneweg. The others (KLR-8223 through KLR-8227) are sub-samples from KLR-8007. KLR-8007 is a bulk sample, i.e. consisting of a mixture of all four grain types. Concerning the description of the grain types refer to Fig. 3.

Sample no.	Description	Analytical techniques applied
KLR-8007	Bulk	GC–MS, Radiocarbon
KLR-8223	White	Raman (Ar), FT-IR, LIBS, XRD, ICP-MS
KLR-8224	Black	Raman (Ar), FT-IR, LIBS, ICP-MS
KLR-8225	Green	Raman (Ar), ICP-MS
KLR-8226	Brown/black	Raman (Ar), Raman (diode), FT-IR, LIBS, ICP-MS
KLR-8227	Black	Proteins

2.2. GC–MS

GC–MS was carried out on a bulk sample of a few milligrams consisting of all four grain types to analyse the organic materials present. The system used was a 6890N GC System Gas Chromatograph from Agilent Technologies coupled with a 5975 Mass Selective Detector (also Agilent Technologies) with a single quadrupole mass spectrometer equipped with a PTV injector. The mass spectrometer was operating in the electron impact (EI) positive mode (70 eV). The MS transfer line temperature was 280 °C; the MS ion source temperature was kept at 230 °C; and the MS quadrupole temperature was 180 °C. The detailed analytical procedure is described in Lluveras et al. (2010). The sample was digested in a microwave oven model MLS-1200 MEGA Milestone. The acidic hydrolysis of proteins was performed using a power of 250 W for 10 min and 500 W for 30 min with 30 mL of 6 N HCl at 160 °C for 40 min. The acidic hydrolysis of polysaccharides was performed using a power of 500 W for 20 min, at 120 °C, with 500 μL of TFA 2M. Saponification was performed using a power of 200 W for 60 min at 80 °C, with 300 μL of KOH in ETOH 10% wt. The detection limit (LOD) and the quantization limit (LOQ) of amino acids, aldoses, uronic acids and fatty and dicarboxylic acids were calculated. At a statistical significance level of 0.05, the LOD and LOQ of the proteinaceous, glycerolipids and saccharide materials were as follows:

- Proteinaceous materials: LOD: 0.2 μg ; LOQ: 0.4 μg
- Glycerolipids: LOD: 1.2 μg ; LOQ: 2.5 μg
- Saccharide materials: LOD: 0.3 μg ; LOQ: 0.6 μg .

2.3. PXRD

Powder X-ray diffraction data were measured at room temperature using a PANalytical X'Pert PRO diffractometer, equipped with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) and a solid-state PIXcel detector (PANalytical B.V., The Netherlands). The samples were mounted between two Kapton foils and measured in transmission geometry over the range 5–70° 2 θ .

2.4. LIBS

Laser-Induced Breakdown Spectroscopy analysis (Miziolek et al., 2006) was performed using the double pulse MODI[®] LIBS Instrument (Bertolini et al., 2006). The instrument uses two Nd:YAG lasers at the fundamental wavelength (1064 nm). One laser pulse was delayed by 1 μs relative to the other. The energy delivered in each laser pulse was around 60 mJ in 10 ns. The analyzed spectra correspond to a single measurement. The plasma signal was collected by an AVANTES spectrometer, with an acquisition gate of 2.48 ms and a delay after the second laser pulse of 2 μs .

2.5. (ATR) FT-IR

The samples were subjected to Attenuated Total Reflection Fourier Transform Infrared spectroscopy (ATR) FT-IR. All FT-IR spectra were recorded with a Spectrum-100 from Perkin Elmer equipped with an ATRU diamond. 64 scans were recorded from each sample with a resolution of 4 cm^{-1} . Acquisition ranged from 600 cm^{-1} to 4000 cm^{-1} .

2.6. Micro-Raman

Micro-Raman measurements were carried out using a Renishaw RM 2000 instrument, coupled with an optical Leica DLML microscope, equipped with a NPLAN objective $50\times$. The laser source was an argon ion laser (Ar^+) with a wavelength of $\lambda = 514.5\text{ nm}$ and a laser power output at the objective of around 2 mW . The spectrometer consists of a single grating monochromator ($1200\text{ lines mm}^{-1}$), coupled with a CCD detector, a RenCam 578×400 pixels ($22\text{ }\mu\text{m} \times 22\text{ }\mu\text{m}$) cooled by a Peltier-element. The spectral calibration of the instrument was performed on the 520.5 cm^{-1} band of a silicon wafer.

2.7. ICP-MS

Minute sub-samples of the ink were analyzed by ICP-MS. Each sample (white, green, black, and brown/black grains) was re-suspended in 1 mL of Milli-Q water and digested in acid in a microwave oven (Milestone Ethos 900-Mega II), in a Teflon vessel by adding a mixture of 4 mL of $67\text{--}69\%$ HNO_3 , 2 mL of 40% HF and 1 mL of 37% HCl . HNO_3 and HCl were SpS™ grade Super Purity Solvent from Romil, Cambridge, UK. Mineralization was achieved with the following microwave oven program: 20 min to reach $220\text{ }^\circ\text{C}$ at 1400 W ; 15 min at $220\text{ }^\circ\text{C}$ and 1400 W ; ventilation for 30 min . The solution was then quantitatively transferred into polystyrene liners and stored at $+4\text{ }^\circ\text{C}$ until the ICP-MS analysis was performed.

The analyses were carried out in triplicate on an Agilent 7700 ICP-MS, equipped with a frequency-matching RF generator and 3rd generation Octopole Reaction System (ORS³), operating with helium as cell gas on diluted samples ($1:10\text{ v/v}$ Milli-Q water). The parameters were set as follows: radiofrequency power 1550 W , plasma gas flow 14 L min^{-1} ; carrier gas flow 0.99 L min^{-1} ; He gas flow 4.3 mL min^{-1} . The Octopole Reaction System was activated to improve the metal quantification because of the interferences by polyatomic species produced by a combination of isotopes coming from plasma, reagents and matrix. ^{103}Rh was used as an internal standard ($50\text{ }\mu\text{g mL}^{-1}$ final concentration). Multi-element calibration standards were prepared in 5% HNO_3 at 4 different concentrations ($1, 10, 50$, and $100\text{ }\mu\text{g L}^{-1}$). The standard addition approach for calibration on 4 concentration levels was used in order to keep the matrix-induced variations to a minimum. At least three replicates of each calibration standard were run. Moreover, in order to correct possible instrumental drifts, ^{103}Rh was added as internal standard to all the samples and calibration standards. It should be noted that the samples were analyzed by two different analytical techniques, LIBS and ICP-MS, in order to monitor possible sample inhomogeneity.

2.8. Proteomic analyses

The identification of the proteinaceous material in the ink sample was carried out following the same proteomic analytical procedure described previously (Leo et al., 2009), except for a preliminary incubation of the sample in strongly protein denaturing conditions (6M urea) that was introduced in order to favour

the exposure of the proteinaceous material to the action of proteases.

A black sub-sample, KLR-8227, of ca $500\text{ }\mu\text{g}$ was digested in an enzymatic reaction by proteomics-grade trypsin. A pre-treatment of the solid sample with 6M urea was carried out by incubation for 1 h in $20\text{ }\mu\text{L}$ followed by sonication for 30 min at room temperature. The sample was then 6-fold diluted with ammonium bicarbonate 10 mM pH 7.5 and enzymatic digestion carried out by addition of $1\text{ }\mu\text{g}$ of trypsin at $37\text{ }^\circ\text{C}$ for 16 h . The supernatant was then recovered by centrifugation and the peptide mixture was concentrated and purified using a reverse-phase C18 Zip Tip pipette tip (Millipore). The peptides were eluted with $20\text{ }\mu\text{L}$ of a solution made of 50% acetonitrile, 0.1% formic acid in Milli-Q water and analyzed by LC–MS/MS.

The peptide mixtures were analyzed using a CHIP MS 6520 QTOF mass spectrometer equipped with a capillary 1200 HPLC system and a chip cube (Agilent Technologies, Palo Alto, CA). After loading, the peptide mixture ($8\text{ }\mu\text{L}$ in 0.1% formic acid) was first concentrated and washed at $4\text{ }\mu\text{L min}^{-1}$ in 40 nL enrichment column (Agilent Technologies chip), with 0.2% formic acid in 2% acetonitrile as eluent. The sample was then fractionated on a C18 reverse-phase capillary column ($75\text{ }\mu\text{m} \times 43\text{ mm}$ in the Agilent Technologies chip) at flow rate of 400 nL min^{-1} with a linear gradient of eluent B (0.2% formic acid in 95% acetonitrile) in A (0.2% formic acid in 2% acetonitrile) from 7 to 60% in 50 min .

2.9. Carbon isotopes and attempts at radiocarbon dating

Radiocarbon dating was attempted on two samples at the Groningen AMS facility in The Netherlands, as described in detail in van der Plicht et al. (2000). The first sample was not pre-treated in any way, i.e. without the usual AAA pre-treatment procedure (acid–alkaline–acid). The second was treated with 4% HCl at room temperature in order to remove carbonates. The samples were combusted to CO_2 and transformed into graphite for AMS measurement (Aerts-Bijma et al., 2001). The stable isotope ratios $\delta^{13}\text{C}$ were measured on an elemental analyser/isotope ratio mass spectrometer (Fisons Instruments EA/IRMS) (Aerts-Bijma et al., 2001).

3. Results

3.1. GC–MS

The combined GC–MS analytical procedure allows identification of glycerolipids (linseed oil, walnut oil, poppy seed oil, and egg), natural waxes (beeswax and Carbauba wax), proteinaceous materials (animal glue, milk or casein, egg, and garlic), plant resins (such as Pinaceae resin, mastic, dammar, and sandarac) and animal resins (shellac), and polysaccharide materials (such as starch, tragacanth gum, arabic gum, fruit tree gum, guar gum, or karaya gum) in the same micro sample (Lluveras et al., 2010). The procedure is based on a multi-step chemical pre-treatment entailing solvent extractions and microwave-assisted chemolysis of the sample, in order to separate three fractions: an amino acidic, a lipid-resinous, and a saccharide fraction. The amino acids in KLR-8007 were at the quantization limit, and the relative content of the sample analyzed is shown in Table 2.

The absence of hydroxyproline indicates the absence of animal glue in the sample. To determine the source of the proteinaceous

Table 2
Amino acid relative percentage content of the bulk sample KLR-8007.

Sample	Ala	Gly	Val	Leu	Ile	Ser	Pro	Phe	Asp	Glu	Hyp
KLR-8007	9.2	14.7	8.8	16.0	8.9	6.6	4.9	6.2	10.1	14.7	0.0

material in the sample, the amino acid percentage content was subjected to a multivariate statistical analysis together with a data set of 121 reference samples of animal glue, casein, and egg (whole egg, albumen and yolk) (Bonaduce et al., 2009) using principal component analysis (PCA) (Brereton, 2004). The resulting score plot, presented in Fig. 4, clearly reveals that the sample is located in the egg cluster.

The lipid-resinous fraction of the sample (chromatogram not reported) revealed the presence of small amounts of fatty acids, and some hydroxylated fatty acids (above the detection limit), indicating the presence of traces of a lipid material partially oxidized. The profile cannot be ascribed to either a drying oil or egg lipids (Colombini et al., 2010), and must thus be related to the material used to prepare the black pigment and not to the binder.

The saccharide fraction showed the presence of sugars at the quantization limit. The chromatogram of the saccharide fraction is presented in Fig. 5 and the relative sugar percentage content is listed in Table 3. The presence of arabinose and galactose, together with the absence of xylose and mannose points to the presence of *Gum Arabica* (Llaveras et al., 2010).

3.2. PXRD

The single grain of sample KLR-8223 produced a diffraction pattern that could be matched completely to that of monohydrocalcite, $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ (Fig. 6, Effenberger, 1981). The remaining samples, KLR-8224, KLR-8225 and KLR-8226, did not yield any measurable diffraction pattern. This does not necessarily exclude that the samples are crystalline, since the amount of each sample was significantly smaller than for KLR-8223 and smaller than would usually be examined using this equipment.

3.3. FT-IR, Raman, and LIBS

3.3.1. Sub-sample KLR-8223 (white)

The presence of monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$), which was detected as the only crystalline phase by PXRD, is confirmed by both Raman and FT-IR (Fig. 7). The main monohydrocalcite bands cited in the literature are easily identifiable in the FT-IR spectra:

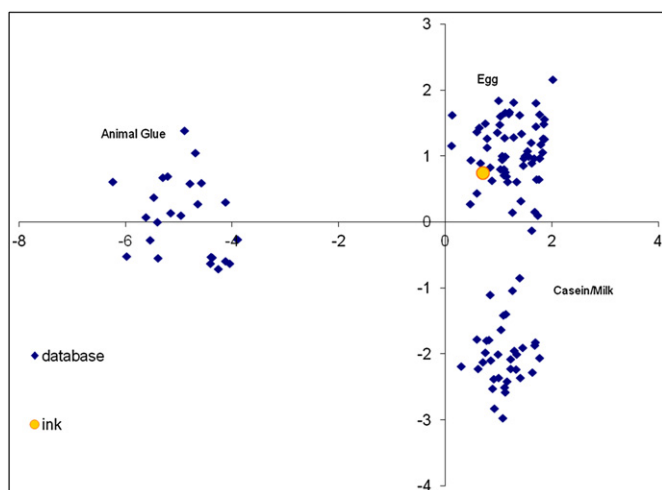


Fig. 4. Results of the GC-MS analyses. The graph shows the principal component analysis score plot of the amino acid relative percentage content of the bulk sample KLR-8007. The PCA analysis was performed using XLstat 6.0 software (Addinsoft, France) on the correlation matrix of the data. The first two components accounted for 82% of the variance in the data. The blue points are database entries for animal glue, egg, and casein. The yellow circle is KLR-8007. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

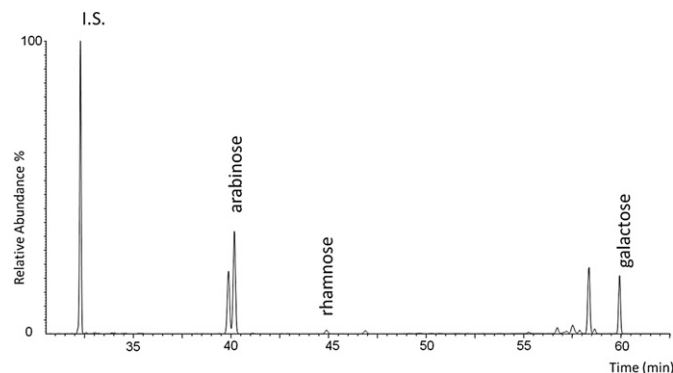


Fig. 5. SIM chromatogram of the saccharide fraction of the bulk sample KLR-8007. The sugars over the detection limit are indicated. I.S. is the internal standard (mannitol).

a strong doublet corresponding to the asymmetric C–O vibrations at 1408 and 1487 cm^{-1} and the bands at 700, 871 and 1067 cm^{-1} corresponding to the carbonate stretching modes. Moreover, the O–H stretching bands at 3225 cm^{-1} and the H_2O deformation band at 1700 cm^{-1} are also observed (Coleyshaw et al., 2003; Neumann and Eppe, 2007; Senorale-Pose et al., 2008; Jones and Jackson, 1993). Calcium is also abundant in the LIBS spectrum (Fig. 8).

3.3.2. Sub-sample KLR-8224 (black)

The Raman spectrum of the black sub-sample KLR-8224 shows the presence of calcium carbonate (CaCO_3) as the main component: the peak at 1087 cm^{-1} is characteristic of calcite (Burgio and Clark, 2001). Calcite is also confirmed by the bands at 1400, 870 and 710 cm^{-1} in the FT-IR spectra (Fig. 9, right), which are characteristic of calcite. The band around 1000 cm^{-1} in the FT-IR spectra has been attributed to the presence of small amounts of silicates in the sample (Pretti and Singh, 2007; Madejova, 2003). However, the presence of a non-intense broad band at around 1550 cm^{-1} in the Raman spectrum of KLR-8224, can be interpreted as the result of the presence of carbon black. When reported in the literature, FT-IR spectrum of the black pigment *vine black* shows an intense band at around 1000 cm^{-1} (Vila et al., 2007). The LIBS spectrum (Fig. 10) shows the organic nature of the sample with a major C peak and a C–N peak. The fact that silicates were not detected by LIBS is attributed to sample inhomogeneity.

3.3.3. Sub-sample KLR-8225 (green)

Sample KLR-8225 was too small to allow analysis by LIBS and FT-IR, therefore only Raman analysis was performed. The Raman spectrum taken from the green grains (Fig. 11) suggests that it is a copper-based green pigment that has suffered degradation. This degradation could be due to the laser light, even though very low laser energy was used for acquisition of the spectrum. A similar degradation phenomenon was seen by Mattei et al. (2008) in the degradation of azurite to tenorite under laser irradiation. The green grain could, however, also have been degraded before the analysis.

3.3.4. Sub-sample KLR-8226 (brown/black)

Both Raman and FT-IR results for sub-sample KLR-8226 show the presence of carbon black. The Raman spectrum (Fig. 12)

Table 3
Glycoside profile of the bulk sample KLR-8007.

Sample	Sugars (% relative)								
	Xyl	Arab	Rham	Fuc	Gal ac	Gluc ac	Gluc	Mann	Galact
KLR-8007	0.0	38.9	5.4	0.0	0.0	0.0	0.0	0.0	55.7

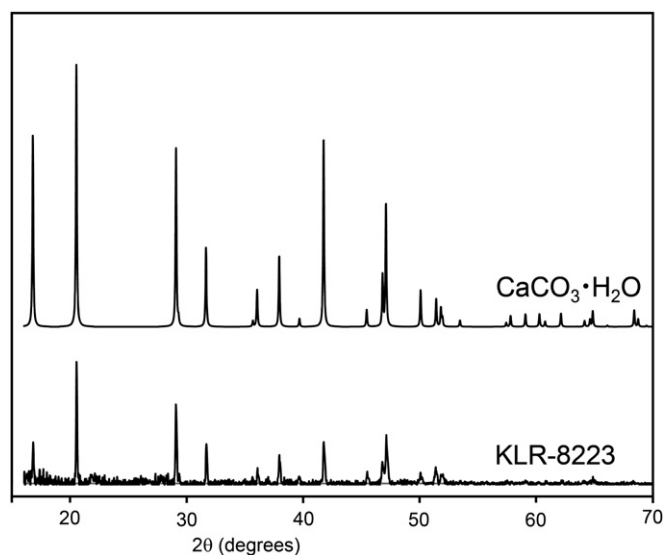


Fig. 6. Powder X-ray diffraction pattern for KLR-8223 in the range 15–70° 2θ, and simulated pattern for monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$) (Effenberger, 1981). There are no diffraction peaks at lower angles. The broad features associated with the background in the region 15–30° 2θ are produced by the Kapton foils.

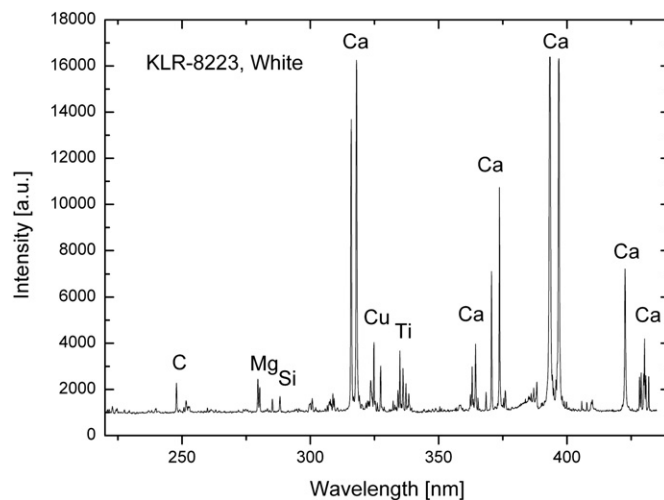


Fig. 8. LIBS spectrum of sub-sample KLR-8223 white.

resembles that of the black pigment reference materials reported by Bell et al. (1997), which lists two broad bands at ca 1325 cm^{-1} and ca 1580 cm^{-1} . It is interesting to note the absence of any band at around 950 cm^{-1} , which would correspond to phosphates. The absence of this band suggests that the sample consists of a lamp black or vine black, as both black pigments are devoid of calcium

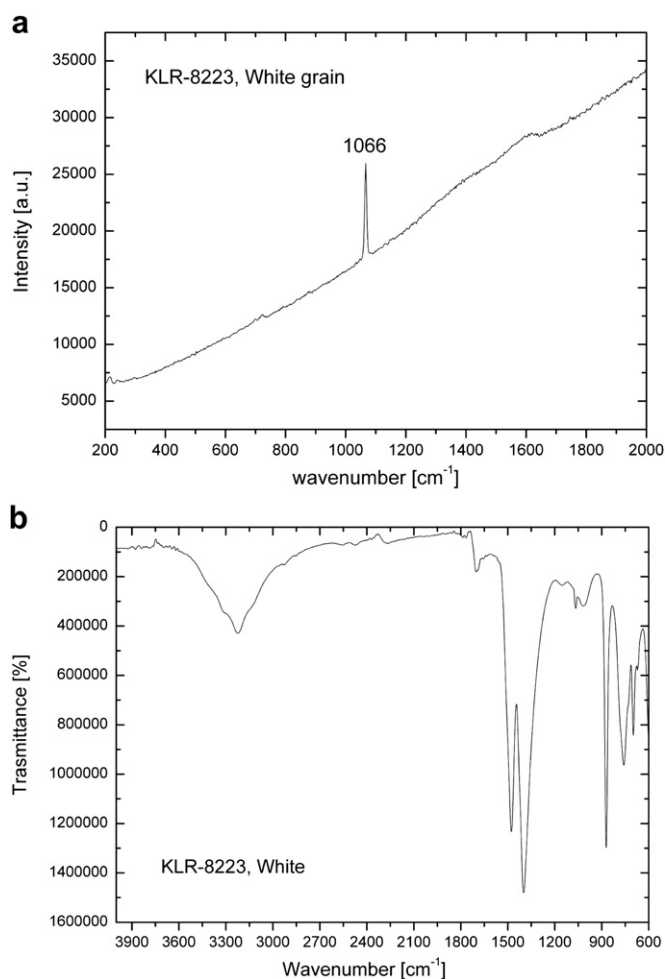


Fig. 7. (a) Raman and (b) FT-IR spectra of sub-sample KLR-8223 white.

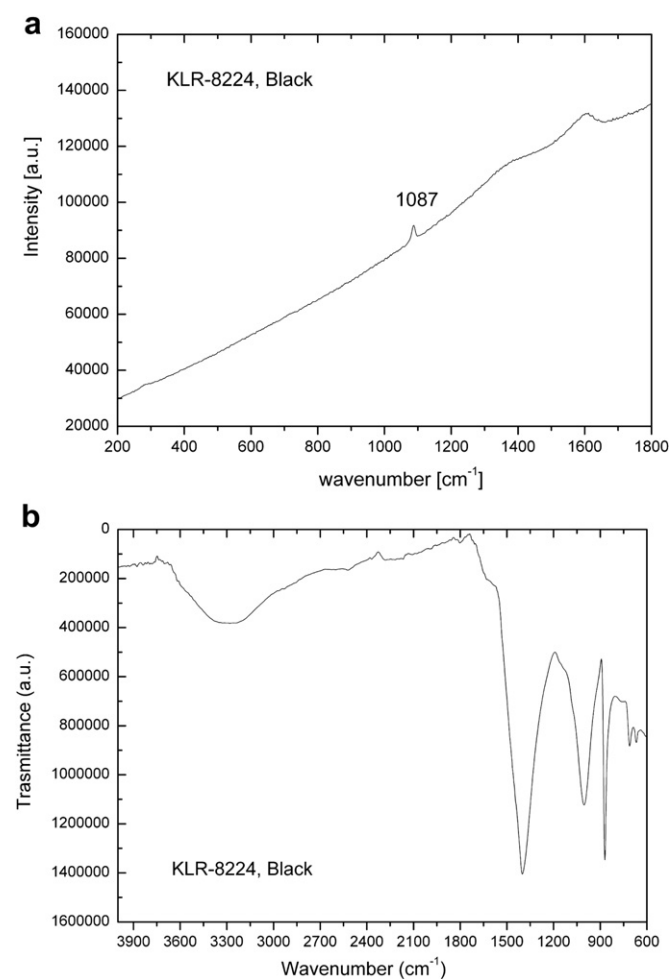


Fig. 9. (a) Raman and (b) FT-IR spectra of sub-sample KLR-8224 black.

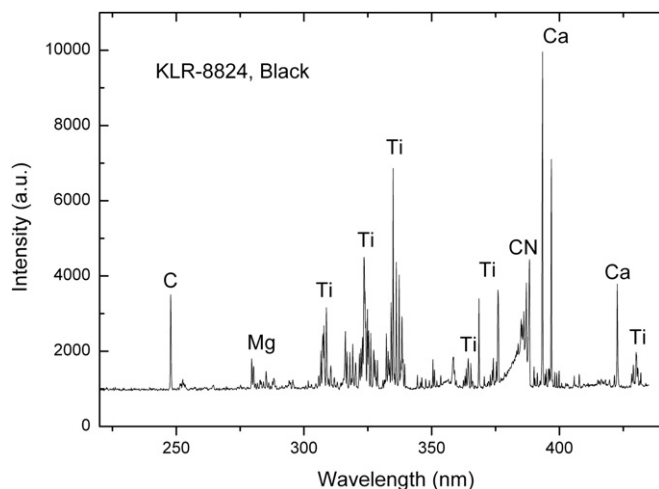


Fig. 10. LIBS spectrum of sub-sample KLR-8224 black.

phosphate (Bell et al., 1997). Moreover, the FT-IR spectrum, showing mainly a band at around 1000 cm^{-1} , resembles closely that of vine black shown in the literature (Vila et al., 2007). Lamp black, containing only amorphous charcoal, does not exhibit any relevant FT-IR signal (Vila et al., 2007). Therefore, the evidence points to vine black as the black pigment in the ink sample, supporting the same identification made for sub-sample KLR-8224, and it definitely excludes the presence of ivory or bone black as these are characterized by the presence of phosphates. Moreover, from the spectra obtained with the diode laser, it is evident that the brown/black grains contain iron-based compounds, which is substantiated by the LIBS spectrum showing a complex mixture of elements: among others Fe, Si, Mg, and Cu (Fig. 13).

3.4. ICP-MS

Intra-day reproducibility was checked by measurements of the sample 3 times on the same day. Inter-day reproducibility was checked by analysis of a similar digested solution on 3 separate days over a period of 1 week. The performance of the ICP-MS analysis is listed in Table 4, and the results of the ink analyses are shown in Table 5.

The Ca-concentration in KLR-8223 corresponds stoichiometrically to a composition of ca 37 wt% monohydrocalcite, which is consistent

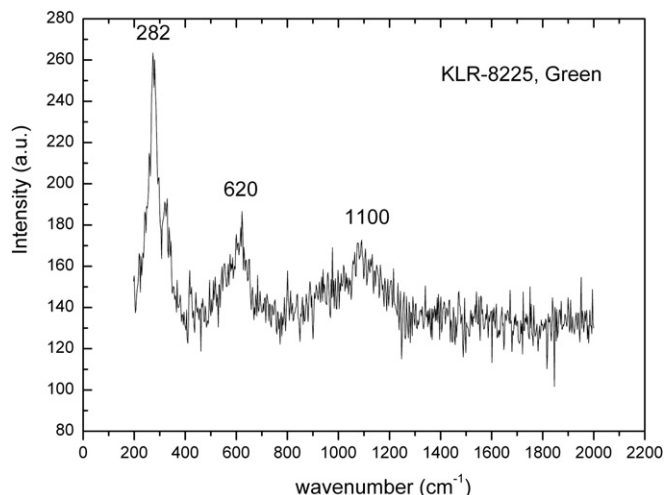


Fig. 11. Raman spectrum for sub-sample KLR-8225 green.

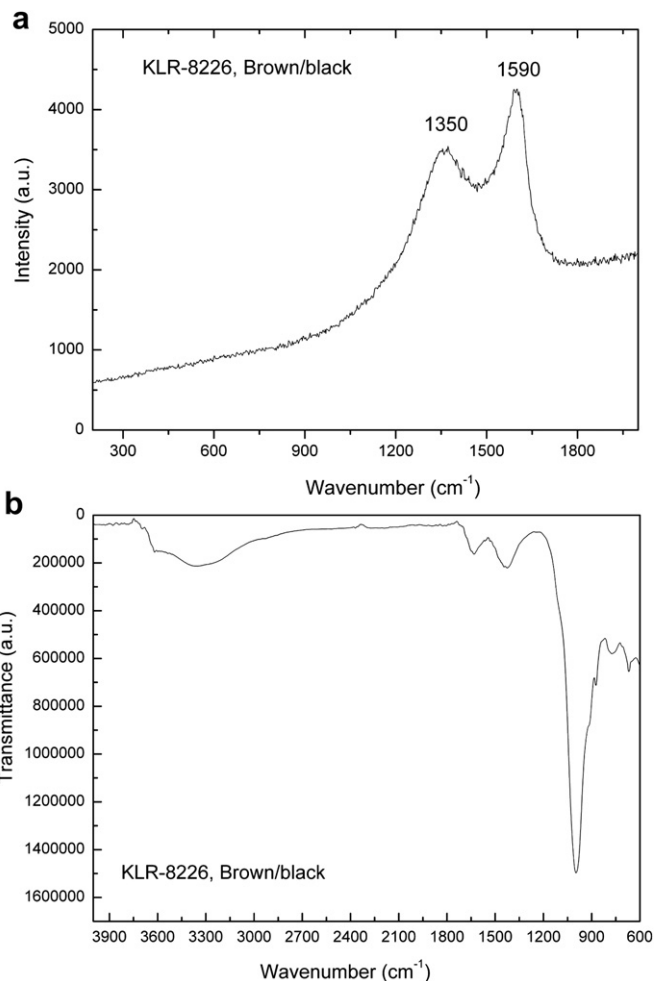


Fig. 12. FT-IR spectra of sub-sample KLR-8226 brown/black obtained with Argon laser (a) and the Raman spectrum (b).

with the LIBS data. Carbon is not analyzed by ICP-MS, but the other elements in the black grain KLR-8224 exhibit more or less even concentrations. The green sample, KLR-8225, has a Ca-concentration corresponding stoichiometrically to ca 25 wt% monohydrocalcite and ca 9 wt% Cu, both of which are consistent with the LIBS data. Besides Ca, the brown/black grain KLR-8226 is high in Al and Fe, indicating the possible presence of clay minerals, which is also in accordance with the other measurements in this study.

3.5. Proteomic analyses

Peptide analysis was performed using data-dependent acquisition of one MS scan (mass range from 400 to 2000 m/z) followed by MS/MS scans of the three most abundant ions in each MS scan. Raw data from nano-LC–MS/MS analyses were used to query non-redundant protein databases (UniprotSprot, either on all entries or with the taxonomy restriction to Chordata) using the MASCOT software (Matrix Science, Boston, USA), without the insertion of any fixed chemical modification but the possible oxidation of methionine and the formation of pyroglutamic acid from glutamine residues at the N-terminal position of peptides. The identification of 4 peptides from chicken ovalbumin allowed confident identification of egg in the sample (Table 6).

As further confirmation of the identification, a residual aliquot (1/5 of the initial sample) was analyzed on LC–MS/MS with a Selected Ion Monitoring program, in order to fragment selectively

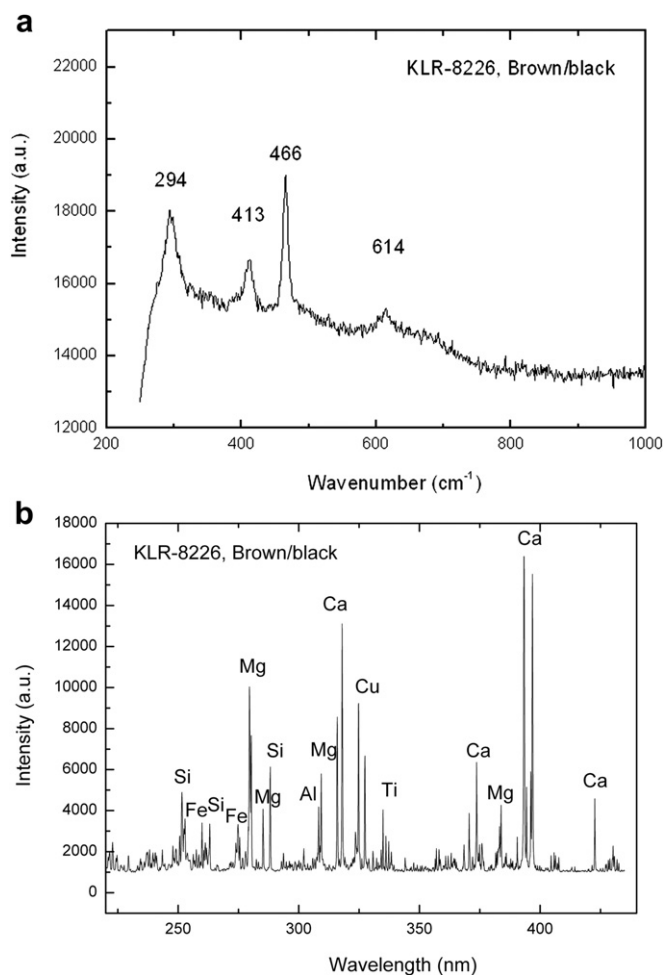


Fig. 13. The FT-IR spectrum obtained with a diode laser (a) and LIBS spectrum (b) of sub-sample KLR-8226 brown/black.

the target ions that had been identified in the previous run. This strategy allowed improvement of the quality of the fragmentation spectra which could all be manually inspected and unambiguously interpreted, and which confirmed the assignment to the peptides inferred above. As an example, in Fig. 14 is shown the fragmentation spectra of the doubly charged ion at 844.42 *m/z* that can be interpreted as the peptide GGLEPINFQTAADQAR spanning from residue G128 to residue R143 of ovalbumin from *Gallus gallus* (P01012).

3.6. Carbon isotopes and attempts at radiocarbon dating

The $\delta^{13}\text{C}$ -values expressed in ‰ deviation from the standard and the carbon content (wt% C) are listed in Table 7. The ^{14}C -age is conventional, i.e. reported in BP (Mook and van der Plicht, 1999). The ^{14}C date is rounded off to the nearest 5, and the error is 1-sigma. The $\delta^{13}\text{C}$ and C% are normally intended as quality parameters for the dated material (van Strydonck et al., 1999).

Table 4

ICP-MS performances in terms of limit of detection (LoD), limit of quantification (LoQ), and intra- and inter-day reproducibility. Limits of detection and quantification are expressed as ng/g, while intra- and inter-day reproducibility values are reported as percentage (%).

Parameter	Al	Cr	Cu	Fe	Mn	Pb	Mg	K	Ca	Ti	Sr
LoD (ng/g)	1.58	0.06	0.46	0.06	0.09	0.08	1.08	1.75	15.9	0.20	0.04
LoQ (ng/g)	1.47	0.16	0.30	78.2	0.10	0.10	3.07	59.7	19.1	0.22	0.16
Intra-day reprod (%)	1.96	3.64	1.44	6.50	4.69	1.39	1.96	3.36	12.8	5.90	3.63
Inter-day reprod (%)	2.15	4.01	1.58	7.15	5.16	1.53	2.16	3.69	14.2	6.49	3.99

Table 5

Quantitative analysis by ICP-MS of a set of the four optically discernable grain types. The concentrations are given in wt%.

	KLR-8223 white	KLR-8224 black	KLR-8225 green	KLR-8226 brown/black
Sample weight (mg)	0.025	0.660	0.030	0.220
Mg	1.71	0.31	2.10	0.17
Al	1.96	0.04	4.82	1.19
K	1.33	0.17	0.82	0.14
Ca	14.76	0.54	8.85	1.12
Ti	1.12	0.03	0.15	0.02
Cr	0.44	0.02	0.35	0.03
Mn	0.07	0.01	0.28	0.01
Fe	2.44	0.50	1.28	0.64
Cu	1.55	1.52	6.62	0.47
Sr	0.26	0.01	0.11	0.02
Pb	0.19	0.19	1.51	0.06
Total wt%	25.82	3.33	26.89	3.87

For reasons explained below we do not believe that the dates reflect the true age of the ink, but rather the combined date of the ink and some contaminants.

4. Discussion

In 2002, Torleif Elgvin and Stephen Pfann noted a further detail that had not previously been reported: according to Kando, the Schøyen inkwell had been found together with a bronze incense altar. Based on comparative parallels of the items, their luxurious nature, and the plausibility that a surface find by the Bedouin would be from an upper layer, Elgvin and Pfann tentatively concluded that the Schøyen inkwell should be attributed to Qumran Period III (although they noted Period II was also possible). Period III is the period of habitation at Qumran defined by the original excavator, Roland de Vaux, to be after the First Jewish Revolt of 66–70 CE. According to de Vaux, Qumran was at this time inhabited by Roman soldiers, after the sectarians believed to be associated with the scrolls had been forced to flee and the site was destroyed by fire (de Vaux, 1973). Virtually all Qumran scholars hold that none of the texts in the caves were produced after the First Revolt. Elgvin and Pfann suggested that Period III was a Jewish habitation, although also unconnected to the scrolls. The notion that Period III Qumran may have been Jewish, not Roman, appears to have first been suggested by Doudna (2001: 744, building from 1999: 39–42). One of the three inkwells found by de Vaux (the one found in locus 36) also was from a Period III context, i.e. also unrelated to the scrolls by the traditional archaeological understanding.

Doudna's argument was as follows: as was noted by Konik (1998), there is no evidence that the inhabitants at Qumran following the Jewish Revolt of 66–70 CE were Romans. No ostraca naming a Roman military commander, no Roman military supplies, or any other sign of Roman occupation have been found at Qumran. The premise of de Vaux's argument for a Jewish/Roman distinction between pre-68 and post-68 Qumran was a distinction between Jewish First Revolt coins and Roman city coins. As de Vaux put it: "these two groups of coins are distributed precisely between two successive levels, the Jewish coins certainly belonging to the lower

Table 6
Identification of the proteins in the ink sample after trypsin digestion and LC–MS/MS analysis. Proteins were identified by searching the UniprotSprot database, with no taxonomy restriction, with MSMS Ion search Mascot software (Matrix Science, http://www.matrixscience.com/help/interpretation_help.html). Ions score is $-10^*Log(P)$, where P is the probability that the observed match is a random event. In this analysis, individual ion scores >35 indicate identity or extensive homology. Protein scores are derived from ion scores as a non-probabilistic basis for ranking protein hits. Only identification of proteins with at least two peptides was considered significant.

Protein (accession number)	Matched sequence (peptide score) (oxidation of methionine, and pyro-Glu formation at Gln at the N-terminus of peptides were inserted as variable modifications in the MS/MS Ion Search Program)	Sequence coverage %	MW
Ovalbumin (P01012)	¹²⁸ GGLEPINFQTAADQAR ¹⁴³ (23) ²⁰¹ VTEQESKPVQMMYQJGLFR ²¹⁹ (39) ¹⁶⁰ NVLQPSSVDSQTAMVLVNAIVFK ¹⁸² (39) ²³⁰ ILELPFASGTMSMLVLLPDEVSGLEQLESIINFEK ²⁶⁴ (22)	24	42,854

level, that of the destruction [Period II], and the Roman coins certainly belonging to the level above this [Period III]...” (1973: 41). This distinction claimed by de Vaux, which was widely repeated in secondary literature, was contradicted by the report of Humbert and Chambon (1994): 306, concerning Qumran locus 40, in which hidden inside the same lamp were found coins now identified as from both the First Revolt and Caesarea of 67/68 CE. Likewise, Roman city coins were found in the same level with Agrippa I coins at loci 8A and 32. It seems that de Vaux’s basis for his Period III argument arose from these early coin identifications which in certain cases were later discovered to be erroneous. Leonard commented correctly that de Vaux’s Period III scheme unravelled almost completely in light of updated published coin identifications (1997: 230). These factors raised the question whether there was a Period III at all.

But in favour of de Vaux’s suggestion that Romans destroyed the site when they arrived in Jericho in 68 CE are arguments from analogy concerning Roman procedures as told by Josephus in War: destroying by fire villages in the neighbourhood of a site taken (War 4.437–438, 443, 446); the strategy of leaving no outpost of rebels in the rear in preparation for a focused siege on Jerusalem (War 4.413, 450); control of roads and passages (War 4.445, 486); and resettling of destroyed sites with deserters to the Romans and assigning them

to rebuild the destroyed or burnt sites (War 4.438, 444, 448). Therefore it is very plausible that the fire at Qumran in 68 CE was caused by the Romans, as de Vaux thought, but the people to whom Qumran was given after the fire need not be the garrison of Roman soldiers of de Vaux’s portrayal. They may have been Jews who previously had deserted to the Roman side (Doudna, 2001: 744).

The suggestion of a Jewish character of Qumran’s Period III was taken up by Elgvin and Pfann (2002) and argued in detail by Taylor (2006). Magen and Peleg (2007: 62) also noted that it seemed “highly unlikely that a Roman garrison would have been stationed at a burned, abandoned site, whose water supply system was no longer operative”. Magness, however, appears to continue to maintain that Qumran Period III was occupied by a garrison of Roman soldiers (Magness, 2002: 62, 2004: 134). A study of Roman inkwells of Khairy (1980) concluded that “the bronze inkwell from Qumran was known elsewhere from about the turn of the Christian era to the second century A.D.” (p. 161).

It should also be noted that Magen Broshi, former curator of the Shrine of the Book, has expressed doubt about the reliability of the antiquities dealer Kando’s information concerning the Schøyen inkwell: “He [Broshi] thinks the items are too beautiful in style to have come from Qumran, and that they more likely derive from a larger Hellenistic site on the East Bank such as Jerash” (Elgvin and

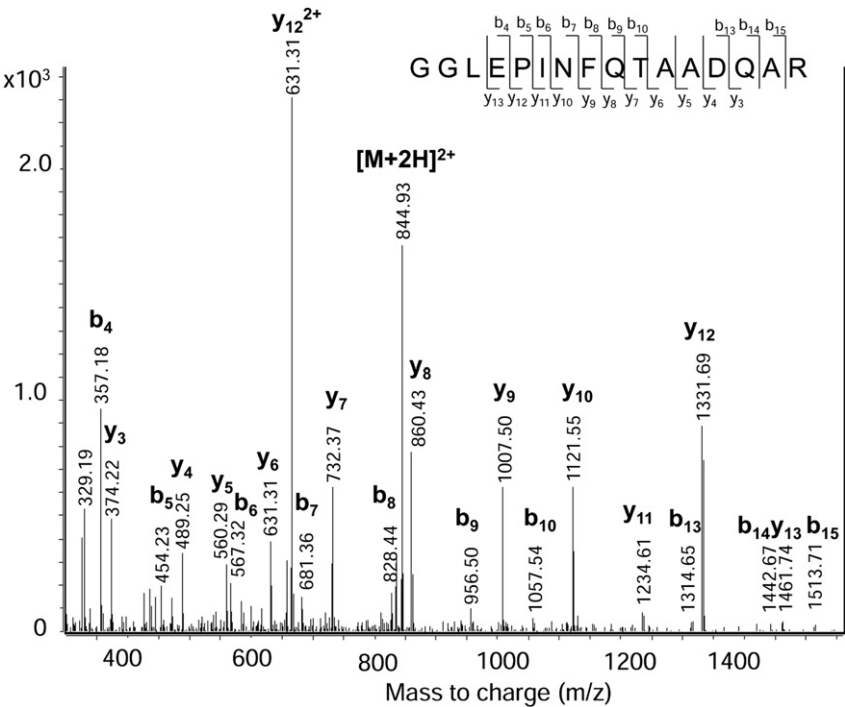


Fig. 14. LC–MS/MS spectrum of the black grain KLR-8227.

Table 7

Results of the stable carbon isotope measurements and the attempts to radiocarbon date the ink.

GrA	Mass used (mg)	Pre-treatment	Age (BP)	1-sigma	$\delta^{13}\text{C}$ (‰ VPDB)	C (wt%)
49,448	7.8	None	2780	50	−19.97	6.0
50,219	21.5	4% HCl at RT	2425	40	−24.04	2.4

Pfann, 2002: 26, citing oral communication with Broshi). But Elgvin and Pfann note that another bronze inkwell which is so similar to the Schøyen inkwell that it “suggests the same manufacturer” was found on the West bank (p. 21). Elgvin and Pfann also note a range of luxury items found at Qumran which appear to be associated with Period III, such that the luxurious Schøyen inkwell would not be out of place. The reported objection of Broshi to the claim of Qumran provenance for the Schøyen inkwell therefore seems insubstantial, and we accept that the Schøyen inkwell originated from Qumran.

What then, about the ink inside the inkwell? None of the analyses in the present work have proven that the ink in the Schøyen inkwell was manufactured at Qumran. Any ink, parchments or other commodity utilized in the Qumran settlement could have been imported. It is possible that the constituents of the ink were imported separately and used together with local Qumran products to produce the ink. However, it is also possible that the ink was manufactured at Qumran with all its components.

It was a priority during this study to radiocarbon date the ink to see if it agreed with the period of habitation at Qumran. However, this goal was not achieved. We suspect that in both dating attempts there remained some contamination in the samples. The $\delta^{13}\text{C}$ of sample GrA-49448 was -19.97‰ VPDB, which is far from the expected value. It is likely that the major part of the carbon in the sample is in the black colour pigment, which is soot produced by burning an organic material under restricted oxygen supply. As has been shown above, the most likely candidate for the soot is vine black. The soot is therefore probably derived from a material which prior to burning is expected to have a $\delta^{13}\text{C}$ -value of -25‰ VPDB. The process of making vine black is likely to produce an isotopic fractionation towards more negative values in the soot, but we have no way of knowing precisely how much more negative than -25‰ VPDB. However, it is clear that the date of the first sample (analyzed before we identified monohydrocalcite by PXRD), was affected by the presence of monohydrocalcite, which is most likely derived from a geological formation of considerable age. We therefore attempted a second radiocarbon date, this time on a pre-treated sample. Experiments on a minute part of the sample showed that a full AAA would dissolve the sample completely, so it was decided to expose the second sample to one acid treatment only (the first A in the AAA). This treatment undoubtedly removed the monohydrocalcite, but even so the $\delta^{13}\text{C}$ was measured to -24.04‰ VPDB, which is more positive than -25 and still more positive than the isotope fractionated soot. We therefore suspect that even after the sample was pre-treated in acid there remained a contaminant with a $\delta^{13}\text{C}$ -value significantly more positive than -25‰ VPDB. We have not been able to identify this contamination. However, one possibility is that it could be tar. Josephus wrote that there were pieces of tar floating in the Dead Sea the size and shape of “headless bulls” (War 4.479 (4.8.3)).

Although our attempts to radiocarbon date the ink have failed, it remains likely—judging from the progression in $\delta^{13}\text{C}$ -values from the untreated sample to the A-treated sample—that the majority of the carbon in the sample is derived from C3 plant material, which would be consistent with the identification of vine black by Raman and FT-IR spectroscopy. Besides the plant-derived carbon, there is a small amount (maybe 5–15 wt%) of organic material with a more positive $\delta^{13}\text{C}$ -value than -25‰ ; a possible candidate for this minor component is tar. We are thus only able to state that the true date of

the ink is younger by an unknown number of years than 750–400 BCE, which is the 2 sigma calibrated date interval of our last dating attempt, but besides this, the dating issue remains unsolved.

The information about the composition of the ink, on the other hand, was unexpectedly rich. The inventory of organic compounds revealed by the GC–MS analysis identified as many as three different compounds: 1) a polysaccharide, *Gum Arabica*; 2) proteins, which were then by proteomic analyses identified as albumen from the eggs of the species *Gallus gallus*; and 3) traces of lipids in the form of fatty and hydroxylated fatty acids, which could have been part of the black colour pigment. A mixture of egg white and arabic gum was thus the binder of the black pigment. Polysaccharide materials, primarily gum arabic, have been used in works of art since antiquity (Laurie, 1911; Doerner, 1934; Mills and White, 1994; Vallance, 1997). Ancient texts on painting techniques cite polysaccharide materials for different purposes (Bonaduce, 2005; Doerner, 1998; Merrifield, 2004; Cennini, 2003). Particularly during the middle ages, polysaccharide materials were used for gilding and in illuminated manuscripts (Bonaduce and Boon, 2008; Bleton et al., 1996). In the Strasburg Manuscript (15th century), the preparation of gum solutions for illuminated manuscripts is described extensively (Doerner, 1998) and they have already been identified in inks (Bleton et al., 1996). The use of albumen is also described as a binder (Mills and White, 1994). The traces of oxidised lipid found are ascribed, most likely, to the residues of the pyrolysis of vine leaves used to prepare the pigment, more than to any binder.

According to Pfann (no date): “Early results of the flotation of materials from an oven in the southern enclosure [of Qumran], excavated in 2002 and sampled again in 2004, includes a fragment of a chicken egg (the author [Pfann] is grateful to Egon Lass for this information)”. In light of this report it is interesting to note that albumen from chicken egg has been identified in the ink from the Schøyen inkwell, as this resource apparently was available at Qumran. While the inventory of organic phases may not be surprising taking each component into consideration individually, the number of them leaves open the very distinct possibility of exact matching of inks with that of the Schøyen inkwell, should analyses of ink samples from the Dead Sea Scrolls or other parchments from the region become available in the future.

The analyses of the four optically distinguishable grain types encompassed microscopic and diffraction examination, the molecular techniques Raman and FT-IR, and elemental analysis by LIBS and ICP-MS. The investigations show that the ink consists of four physically very distinct phases, which can be described as: 1) a white phase consisting mainly of monohydrocalcite; 2) a black organic phase with carbon black, probably vine black, as the black colour pigment and some traces of monohydrocalcite; 3) a green phase consisting of a calcium carbonate matrix discoloured by Cu; and finally 4) a brown/black phase, consisting of carbon black colour pigment and a complex mixture of silicates. The composition of the green phase is consistent with previous analyses from the Norwegian Technical University of the inkwell bronze to 55–68 wt % Cu, 23–39 wt % Pb, and 5–8 wt % Sn; it seems likely that the high Cu values, and possibly also the smaller amounts of Pb, could be due to some chemical reaction taking place over the millennia between the bronze of the inkwell and the monohydrocalcite of the ink allowing Cu from the inkwell walls to diffuse into decomposed monohydrocalcite.

Monohydrocalcite is a rare mineral found in exotic geological settings, e.g. in connection with the decay of ikaite in the arctic waters of Greenland (Dahl and Buchardt, 2006), in the Shiowakka cold saline spring in Japan, where ikaite is deposited in the cold winter months but monohydrocalcite during the summer (Coleyshaw et al., 2003), in Solar Lake on the Sinai coast (Krumbein,

1975), and in South Australian beach rocks (Swainson, 2009). It has also been associated with environments in which evaporation exceeds precipitation such as salt lakes, tropical lagoons, and sabkhas (Fischbeck and Müller, 1971). Monohydrocalcite has been identified as a biomineral (Neumann and Epple, 2007), and in a variety of exotic species, such as woodlice *Porcellio scaber* (Becker et al., 2003), *Porcellio pachydermatina*, from lobster carapace and from plant cystoliths (Levi-Kalishman et al., 2002), in the bacteria *Halobacillus trueperi* (Rivadeneira et al., 2004), and in bladder stones of guinea pigs (Catherine et al., 1977). Even though monohydrocalcite is found in many and very different environments all authorities agree that it is a very rare mineral.

There are no known occurrences of monohydrocalcite near Qumran, in the Judean hills or on the banks of the Dead Sea today, which leaves three possibilities open. The first is that the monohydrocalcite in the ink was imported from elsewhere (e.g. from Solar Lake on the Sinai shoreline). The second is that monohydrocalcite did exist near Qumran at that time but does not today. Hypothetically it is possible that a small epiphemeral lake detached from the Dead Sea in a geologic setting analogous with that of Solar Lake could have existed. The third is that a source of monohydrocalcite does exist in the vicinity of Qumran today but has not yet been discovered or identified. In any event, monohydrocalcite is not a common rock forming mineral and it must have been a very scarce resource also at the time of the main habitation in Qumran. It seems likely that the monohydrocalcite was added as filler, ensuring that the ink obtained the desired opacity.

The black colour pigment in the ink is most likely vine black, situated in the brown/black phase and in the black phase. Vine black is produced as soot made by burning grape vines. Due to the lack of phosphates in the samples, the presence of ivory black or bone black, i.e. soot made from burning bones or antlers can be excluded. It is interesting that fat, bones, and antlers from goats can be eliminated as a source for the black colour pigment, as hides of goats most likely were prepared in a rather complicated industrial process for the production of the parchment on which the Dead Sea Scrolls were written (Bar-Gal et al., 2001, 2010). It would have been straightforward if the bones and antlers of the goats which were available from the production of parchment had been used for the production of ivory black, provided both parchment and ink were made at the site. This was, however, not the case with the ink in the Schøyen inkwell.

It is possible that the black grains are in fact monohydrocalcite grains coated with or saturated with vine black. However, since the black grains contain monohydrocalcite and an organic phase but only minute amounts of silicates and the brown/black grains contain no monohydrocalcite, it is likely that the origin of the two types of grains are distinctly different, i.e. two different phases that were brought together and physically mixed.

The green phase was found to be a calcium carbonate matrix with traces of Cu. We speculate that the green phase could be degradation products of monohydrocalcite that has somehow reacted with the metal inkwell which has Cu as its main constituent. However, it has not been confirmed that the green grains are decomposed monohydrocalcite grains. The green phase could alternatively be yet another independent exotic compound. Even so, a future identification of Cu-discoloured calcium carbonate grains may act as a provenancing tool linking the ink with a metal inkwell such as the present one. As Cu occurs most abundantly in the green phase, and less abundantly in the black and brown/black phases, it seems unlikely that the Cu originated from the production of the black pigment, for instance by scraping the soot off a metallic lamp made of a Cu alloy.

Besides the carbon black, the brown/black phase contains silicates, which, judging from the high Al content could well be

clay minerals. The mineralogical composition has not been established due to the small sample size, but the main element and trace element composition have been documented by the ICP-MS analysis. The pattern of variation between the elements may be used as a fingerprint to match inks from texts written with a similar ink. When looking at the abundances (Fig. 15) it is clear that the elemental fingerprint is quite similar for the black and the brown/black phases with the Al concentration as the only large difference, Al being higher in the brown/black phase. The white and the green phases resemble each other and are distinct from the black and the brown/black phases, but there are several distinct differences between the abundances of the white phase and the green phase, notably in the elements Al, Ti, Mn, and Pb.

The results of our investigation can be compiled into a list of parameters suitable for provenancing or matching the ink if similar analyses of ink on parchments from Qumran or the region become available. Ten compounds or observations listed in Table 8 have been identified that singly or in combination can act as tools for provenancing the ink. This possibility of provenancing the ink of the Dead Sea Scrolls may prove to be a very potent tool capable of solving issues of interest to scholars working on the history of Jewish texts, e.g. the question of whether or not some of the Dead Sea Scrolls were in fact written at Qumran, or were brought there from elsewhere, e.g. Jerusalem, Jericho, or Damascus.

In terms of industrial processes, handicrafts, or other information pertinent to the people inhabiting Qumran (which would be relevant under the hypothesis that the ink was manufactured at Qumran), the following items have been identified:

- 1) The raising of chickens (*Gallus gallus*).
- 2) The procurement of *Gum Arabica*.
- 3) The production or procurement of the black colour pigment vine black.
- 4) The procurement of the rare mineral monohydrocalcite.

The presence of—or agreement with—the ten parameters mentioned above in another ink, such as e.g. on a Dead Sea Scroll, cannot in itself provenance the ink to Qumran. What the ten parameters can do is match ink from a specific text to the producer of the ink in the Schøyen inkwell, whether the place of production of that ink was Qumran or some other site. The methodology may, however, provide unique information pertinent to assignment of scribal hands.

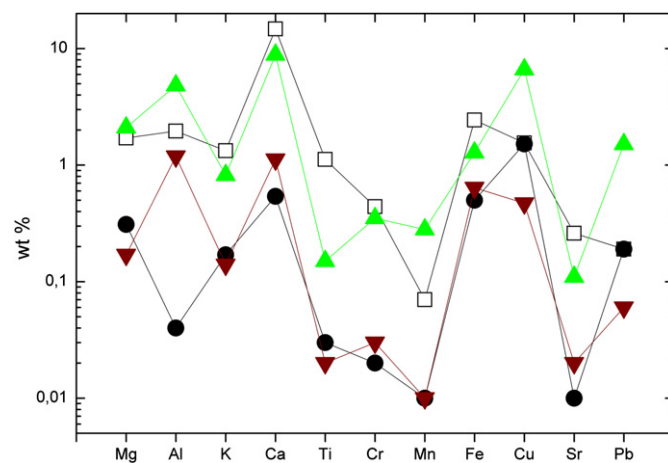


Fig. 15. Fingerprint of elemental abundances measured by ICP-MS. Squares: white grain KLR-8223; circles: black grain KLR-8224; pyramids: green grain KLR-8225; triangle on the tip: brown/black grain KLR-8226. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 8

Ten diagnostic components in or observations about the ink which can be used to diagnose provenance in the ink of parchments.

Diagnostic component	Techniques used
1 4 optically distinct grain types: white, black, green, and brown/black	Microscope
2 Monohydrocalcite in the white grains	PXRD, Raman, FT-IR
3 Proteins, albumen of <i>Gallus gallus</i>	GC–MS, Proteins
4 Polysaccharides, <i>Gum Arabica</i>	GC–MS
5 Fatty acids and hydroxylated fatty acids	GC–MS
6 Black colour pigment with no phosphates, probably vine black	Raman, FT-IR
7 C3 plant material present in the non-carbonate carbon	MS
8 Copper in a carbonate matrix in the green grains	Raman, LIBS
9 Aluminium in the brown/black grains	LIBS, ICP-MS
10 Distinct trace element compositional fingerprint of the 4 grain types	ICP-MS

5. Conclusions

An entirely new insight has been obtained concerning the composition of the ink from the Schøyen inkwell, which could have been used in the *scriptorium* at Qumran. Ten distinct, recognizable and diagnostic parameters of the ink have been identified: (1) the ink contains four different and easily recognizable grain types: white, green, black, and brown/black; (2) the white grains are identified as the rare mineral monohydrocalcite, which is not found naturally near the Dead Sea, and therefore provides a highly specific link to Qumran; (3) the green phase consists of a degraded carbonate matrix discoloured by copper; (4) the colour pigment in the black phase can probably be identified as vine black; (5) the brown/black grains contain aluminium, probably from clay minerals; (6) protein analysis shows that albumen of *Gallus gallus* (chicken) is present in the ink as a binder; (7) *Gum Arabica*, a polysaccharide binder, is also present; (8) fatty acids and hydroxylated fatty acids are present, hypothetically as part of the black colour pigment; (9) the bulk of the organic carbon most likely originated from C3 plant material with a $\delta^{13}\text{C}$ -value of -25‰ VPDB; (10) the ink shows a characteristic elemental concentration pattern that can be used as a fingerprint for each of the four grain types.

These ten parameters constitute a new and potent tool for matching parchments which were inscribed with the same unique ink. This study therefore opens, for the first time, an opportunity to establish the provenance of ink on Dead Sea Scrolls and other manuscripts from Israel and the Levant at the time of main habitation at Khirbet Qumran.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at doi:10.1016/j.jas.2012.04.041.

References

- Aerts-Bijma, A.T., van der Plicht, J., Meijer, H.A.J., 2001. Automatic AMS sample combustion and CO₂ collection. *Radiocarbon* 43, 293–298.
- Bar-Gal, G.K., Rosenberg, T., Greenblatt, C., 2010. Animal remains from Khirbet Qumran: a case study of two bones (QUM 392 and 393) from two bone burials.

- In: Gunneweg, Jan, Adriaens, Annemie, Dik, Joris (Eds.), *Holistic Qumran: Trans-disciplinary Research of Qumran and the Dead Sea Scrolls. Studies on the Texts of the Desert of Judah*, vol. 87. Brill, Leiden, pp. 67–76.
- Bar-Gal, G.K., Greenblatt, C., Woodward, S.R., Broshi, M., Smith, P., 2001. The genetic signature of the Dead Sea Scrolls. In: Goodblatt, David, Pinnick, Avital, Schwartz, Daniel R. (Eds.), *Historical Perspectives: From the Hasmoneans to Bar Kokhba in Light of the Dead Sea Scrolls. Proceedings of the Fourth International Symposium of the Orion Center for the Study of the Dead Sea Scrolls and Associated Literature*, 27–31 January 1999. Studies on the Texts of the Desert of Judah, vol. 37. Brill, Leiden, pp. 165–171.
- Becker, A., Bismayer, U., Epple, M., Fabritius, H., Hasse, B., Shi, J., Ziegler, A., 2003. Structural characterisation of X-ray amorphous calcium carbonate (ACC) in sternal deposits of the crustacea *Porcellio scaber*. *Dalton Transactions*, 551–555.
- Bell, I.M., Clark, R.J.H., Gibbs, P.J., 1997. Raman spectroscopic library of natural and synthetic pigments. *Spectrochimica Acta Part A* 53 (12), 2159–2179.
- Bertolini, A., Carelli, G., Francesconi, F., Francesconi, M., Marchesini, L., Marsili, P., Sorrentino, F., Cristoforetti, G., Legnaioli, S., Palleschi, V., Pardini, L., Salvetti, A., 2006. Modi: a new mobile instrument for in situ double-pulse LIBS analysis. *Analytical and Bioanalytical Chemistry* 385, 240–247.
- Bleton, J., Coupry, C., Sansouet, J., 1996. Approche d'étude des encres anciens. *Studies in Conservation* 41 (2), 95–108.
- Bonaduce, I., 2005. A multi-analytical approach for the investigation of materials and techniques in the art of gilding. Unpublished PhD thesis, Università di Pisa.
- Bonaduce, I., Boon, J.J., 2008. An integrated mass spectrometric and molecular imaging analytical approach to identify and localise constituents in paintings applied to gilded multilayer structures from the 14th to 16th C works of art. In: Colombini, M.P., Tassi, L. (Eds.), *New Trends in Analytical, Environmental and Cultural Heritage Chemistry. Transworld Research Network*, pp. 345–388.
- Bonaduce, I., Cito, M., Colombini, M.P., 2009. The development of a gas chromatographic–mass spectrometric analytical procedure for the determination of lipids, proteins and resins in the same paint micro-sample avoiding interferences from inorganic media. *Journal of Chromatography A* 1216, 5931–5940.
- Brereton, R.G., 2004. *Chemometrics Data Analysis for the Laboratory and Chemical Plant*. J. Wiley & Sons Ltd, West Sussex, England.
- Burgio, L., Clark, R.J.H., 2001. Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation. *Spectrochimica Acta Part A* 57, 2231–2239.
- Catherine, H., Skinner, W., Osbaldiston, G.W., Wilner, A.N., 1977. Monohydrocalcite in a guinea pig bladder stone, a novel occurrence. *American Mineralogist* 62 (3–4), 273–277.
- Cennini, C., 2003. In: Frezzato, F. (Ed.), *Il libro dell'Arte*, first ed. Neri Pozza Editore, Vicenza.
- Coleyshaw, E.E., Crump, G., Griffith, W.P., 2003. Vibrational spectra of the hydrated carbonate minerals ikaite, monohydrocalcite, lansfordite and nesquehonite. *Spectrochimica Acta Part A* 59, 2231–2239.
- Colombini, M.P., Andreotti, A., Bonaduce, I., Modugno, F., Ribechini, E., 2010. Analytical strategies for characterizing organic paint media using gas chromatography/mass spectrometry. *Accounts of Chemical Research* 43, 715–727.
- Dahl, K., Buchardt, B., 2006. Monohydrocalcite in the Arctic Ikka Fjord, SW Greenland: first reported marine occurrence. *Journal of Sedimentary Research* 76, 460–471.
- Doerner, M., 1934. *The Materials of the Artist and Their Use in Painting*. Harcourt, Brace, New York. 223–224.
- Doerner, M., 1998. *Los materiales de pintura y su empleo en el arte*, 18ª edición. Editorial Reverté, Barcelona.
- Doudna, G., 1999. Redating the Dead Sea Scrolls Found at Qumran. *Qumran Chronicle* 8 [special issue, Dec. 1999]. Enigma Press, Cracow.
- Doudna, G., 2001. 4Q Pesher Nahum. A Critical Edition. *JSPS* 35. Sheffield Academic Press, Sheffield.
- Effenberger, H., 1981. Kristallstruktur und Infrarot- Absorptionsspektrum von synthetischem Monohydrocalcite, CaCO₃·H₂O. *Monatshefte für Chemie* 112, 899–909.
- Elgvin, T., in collaboration with S. Pfann, 2002. An incense altar from Qumran? *Dead Sea Discoveries* 9 (1), 20–33.
- Fischbeck, R., Müller, G., 1971. Monohydrocalcite, hydromagnesite, nesquehonite, dolomite, aragonite, and calcite in speleothems of the Fränkische Schweiz, Western Germany. *Contributions to Mineralogy and Petrology* 33 (2), 87–92.
- Goranson, S., 1992. An inkwell from Qumran. *Michmanim* 6, 37–40.
- Goranson, S., 1993. Qumran: the evidence of the inkwells. *Biblical Archaeology Review* 19 (6), 67.
- Goranson, S., 1994. A hub of scribal activity? *Biblical Archaeology Review* 20 (5), 37–39.
- Humbert, J.-B., Chambon, A. (Eds.), 1994. *Fouilles de Khirbet Qumrân et de 'Ain Feskha. Album de photographies. Répertoire du fonds photographiques. Synthèse des notes de chantier du Père Roland de Vaux*, NTO.ASA 1, vol. 1. Editions Universitaires-Vandenhoeck & Ruprecht, Fribourg-Göttingen.
- Jones, G.C., Jackson, B., 1993. *Infrared Transmission Spectra of Carbonate Minerals*. Chapman & Hall, Glasgow, UK.
- Khairy, N.I., 1980. Inkwells of the Roman Period From Jordan. *Levant*. 155–162.
- Konik, J., 1998. Qumran – the analysis of the chronology and the attempt to define the character of the building. *Qumran Chronicle* 8, 105–107.

- Krumbein, W.E., 1975. Biogenic monohydrocalcite spherules in lake sediments of Lake Kivu (Africa) and the Solar Lake (Sinai). *Sedimentology* 22, 631–634.
- Laurie, A.P., 1911. *The Materials of the Painters' Craft*. J.B. Lippincott, Philadelphia. 164 p.
- Leo, G., Cartechini, L., Pucci, P., Sgamellotti, A., Marino, G., Birolo, L., 2009. Proteomic strategies for the identification of proteinaceous binders in paintings. *Analytical and Bioanalytical Chemistry* 395, 2269–2280.
- Leonard, R.D., 1997. Numismatic evidence for the dating of Qumran (review article). *Qumran Chronicle* 7, 225–234.
- Levi-Kalishman, Y., Raz, S., Weiner, S., Addadi, L., Sagi, I., 2002. Structural differences between biogenic amorphous calcium carbonate phases using X-ray absorption spectroscopy. *Advanced Functional Materials* 12 (1), 43–48.
- Llucheras, A., Bonaduce, I., Andreotti, A., Colombini, M.P., 2010. A GC/MS analytical procedure for the characterization of glycerolipids, natural waxes, terpenoid resins, proteinaceous and polysaccharide materials in the same paint micro sample avoiding interferences from inorganic media. *Analytical Chemistry* 82, 376–386.
- Madejova, J., 2003. FT-IR techniques in clay mineral studies. *Vibrational Spectroscopy* 31, 1–10.
- Magen, Y., Peleg, Y., 2007. *The Qumran Excavations 1993–2004: Preliminary Report*. IAA, Jerusalem.
- Magness, J., 2002. *The Archaeology of Qumran and the Dead Sea Scrolls*. Eerdmans, Grand Rapids, Michigan.
- Magness, J., 2004. *Debating Qumran. Collected Essays on its Archaeology*. Peeters, Leuven.
- Mantouvalou, I., Wolff, T., Hahn, O., Rabin, I., Lühl, L., Pagels, M., Malzer, W., Kanngiesser, B., 2011. 3D micro-XRF for cultural heritage objects: new analysis strategies for the investigation of the Dead Sea Scrolls. *Analytical Chemistry* 83, 6308–6315.
- Mattei, E., de Vivo, G., De Santis, A., Gaetani, C., Pelosi, C., Santamaria, U., 2008. Raman spectroscopic analysis of azurite blackening. *Journal of Raman Spectroscopy* 39, 302–306.
- Merrifield, M.P., 2004. *The Art of Fresco Painting in the Middle Ages and the Renaissance*. Courier Dover Publications, ISBN 0486432939.
- Mills, J., White, R., 1994. *The Organic Chemistry of Museum Objects*, second ed. Butterworth Heineman, London.
- Miziolek, A.W., Palleschi, V., Schechter, I., 2006. In: *Laser Induced Breakdown Spectroscopy*. Cambridge University Press.
- Mook, W.G., van der Plicht, J., 1999. Reporting ^{14}C activities and concentrations. *Radiocarbon* 41, 227–239.
- Neumann, M., Eppe, M., 2007. Monohydrocalcite and its relationship to hydrated amorphous calcium carbonate in biominerals. *European Journal of Inorganic Chemistry*, 1953–1957.
- Nir-El, Y., Broshi, M., 1996. Black ink of the Qumran Scrolls. *Dead Sea Discoveries* 3 (2), 157–167.
- Pfann, S., no date. *A Table Prepared in Wilderness: Pantries and Tables, Pure Food and Sacred Space at Qumran*. <http://www.uhl.ac/articles/TableInWilderness.pdf>.
- van der Plicht, J., Wijma, S., Aerts, A.T., Pertuisot, M.H., Meijer, H.A.J., 2000. Status report: the Groningen AMS facility. *Nuclear Instruments and Methods in Physics Research B* 172, 58–65.
- Pretti, S.N., Singh, B.K., 2007. Instrumental characterization of clay by XRF, XRD and FT-IR. *Bulletin of Material Science* 30 (3), 235–238.
- Rabin, I., Hahn, O., Wolff, T., Masic, A., Weinberg, G., 2009. On the origin of the ink of the thanksgiving scroll (1QHodayota). *Dead Sea Discoveries* 16, 97–106.
- Rivadeneira, M.A., Parraga, J., Delgado, R., Ramos-Cormenzana, A., Delgado, G., 2004. Biomineralization of carbonates by *Halobacillus trueperi* in solid and liquid media with different salinities. *FEMS Microbiology Ecology* 48, 39–46.
- Senorale-Pose, M., Chalar, C., Dauphin, Y., Massard, P., Pradel, P., Mariin, M., 2008. Monohydrocalcite in calcareous corpuscles of *Mesocostoides corti*. *Experimental Parasitology* 118, 54–58.
- Steckoll, S., 1968. Investigation of the inks used in writing the Dead Sea Scrolls. *Nature* 220, 91–92.
- Steckoll, S., 1969. An inkwell from Qumran. *Mada* 13, 260–261 [in Hebrew].
- van Strydonck, M., Nelson, D.E., Combre, P., Bronk Ramsey, C., Scott, E.M., van der Plicht, J., Hedges, R.E.M., 1999. What's in a ^{14}C date. In: *Actes du 3ème Congrès International ^{14}C et Archéologie*, Lyon, 6–10 avril 1998, 433–448. *Mémoires de la Société Préhistorique Française*, vol. 26.
- Swainson, I.P., 2009. The structure of monohydrocalcite and the phase composition of the beachrock deposits of Lake Butler and Lake Fellmongery, South Australia. *American Mineralogist* 93 (7), 1014–1018.
- Taylor, J., 2006. Khirbet Qumran in period III. In: Galor, Katharina, Humbert, Jean-Baptiste, Zangenberg, Jürgen (Eds.), *Archaeological Interpretations and Debates. Proceedings of a Conference Held at Brown University, November 17–19 2002*. Brill, Leiden, pp. 133–146.
- Vallance, S.L., 1997. Applications of chromatography in art conservation: techniques used for the analysis and identification of proteinaceous and gum binding media. *Analyst* 122, 75R–81R.
- de Vaux, R., 1973. *Archaeology and the Dead Sea Scrolls: the Schweich Lectures of the British Academy 1959*. Oxford University Press, Oxford.
- Vila, A., Ferrer, N., Garcia, J.F., 2007. Chemical composition of contemporary black printing inks based on infrared spectroscopy: basic information for the characterization and discrimination of artistic prints. *Analytica Chimica Acta* 591, 97–105.